Lecture 9

Mass transfer theories

Intended Learning Outcomes

- Analysis of some more problems applying mass transfer correlations.
- Apply three different mass transfer theories to understand dependence on mass transfer coefficient on diffusivity and velocity.
- Understand why mass transfer theories, specially related to fluid-fluid interface in predicting the mass transfer coefficient?

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In-class exercise problem 1

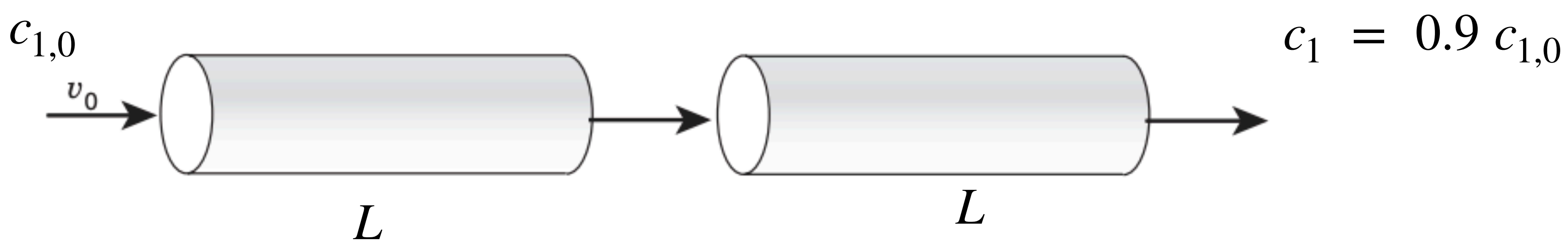
You are responsible for the fabrication of a sensor involving patterning Si wafer with the aid of a 540 nm thick polymer film (photoresist). In the last step, the photoresist needs to be removed. The process involves soaking the photoresist in a large reservoir of organic solvent. You noticed that the photoresist dissolves in 10 minutes. Calculate the mass transfer coefficient.

The solubility of photoresist in the solvent is 2.23×10^{-3} g/cm^3.
The density of photoresist is 0.96 g/cm^3.

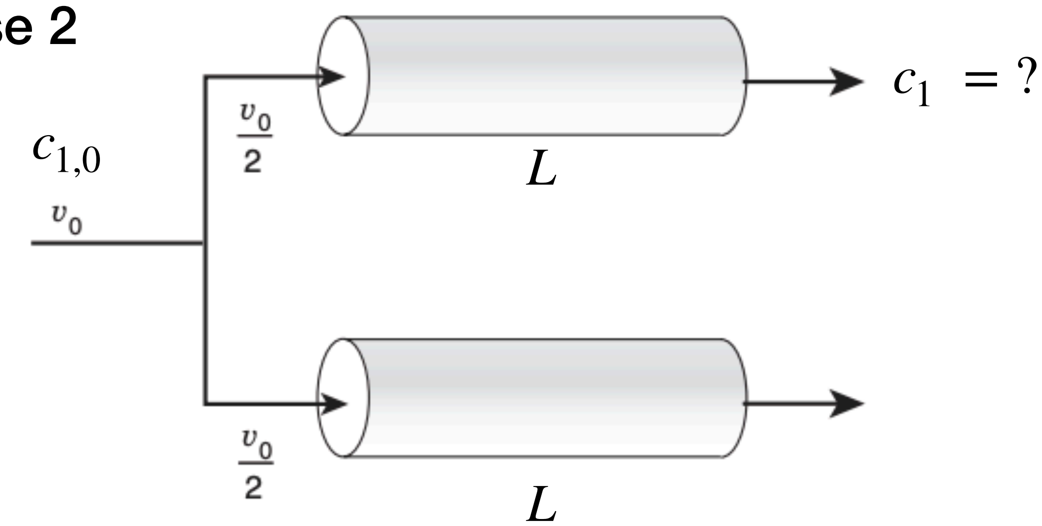
In-class exercise problem 2

Compare the two cases with irreversible reaction in packed bed and calculate c_1 in case 2.

Case 1



Case 2



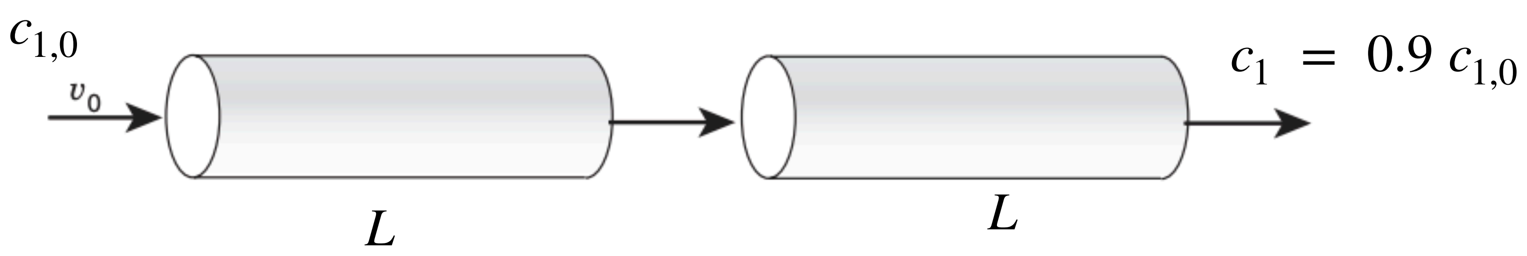
$$\frac{k}{v^0} = 1.17 \left(\frac{dv^0}{\nu}\right)^{-0.42} \left(\frac{D}{\nu}\right)^{2/3}$$

$$c_1 = c_{1,0} \exp\left(-\frac{kaz}{v}\right)$$

In-class exercise problem 2

Compare the two cases with irreversible reaction in packed bed and calculate c_1 in case 2.

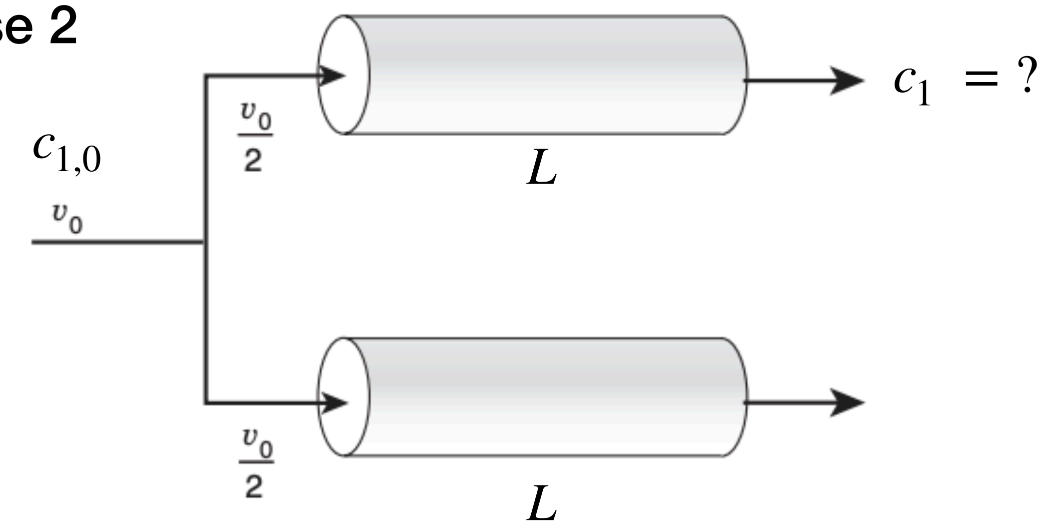
Case 1



In-class exercise problem 2

Compare the two cases with irreversible reaction in packed bed and calculate c_1 in case 2.

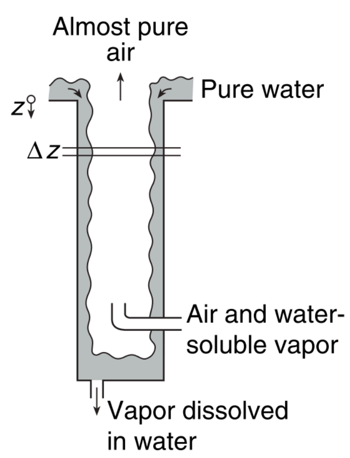
Case 2



Can we derive correlations from first-principle?

Fluid-fluid interface

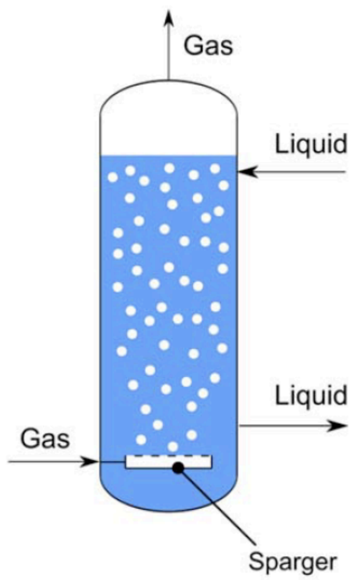
Falling film



$$\frac{kz}{D} = 0.69\left(\frac{zv}{D}\right)^{0.5}$$

$$k \sim D^{0.5}, \quad \sim v^{0.5}$$

Gas bubbles in tank



Source: Wikipedia, "Blasensäule"

$$\frac{kd}{D} = 0.31\left(\frac{d^3 g \Delta\rho}{\rho \nu^2}\right)^{1/3}\left(\frac{\nu}{D}\right)^{1/3}$$

$$k \sim D^{2/3}$$

Liquid in packed tower

Source: Büchi Glas, Uster

$$k\left(\frac{1}{\nu g}\right)^{1/3} = 0.0051\left(\frac{v^0}{a\nu}\right)^{0.67}\left(\frac{D}{\nu}\right)^{0.5}(ad)^{0.4}$$

$$k \sim D^{0.5}, \quad \sim v^{0.67}$$

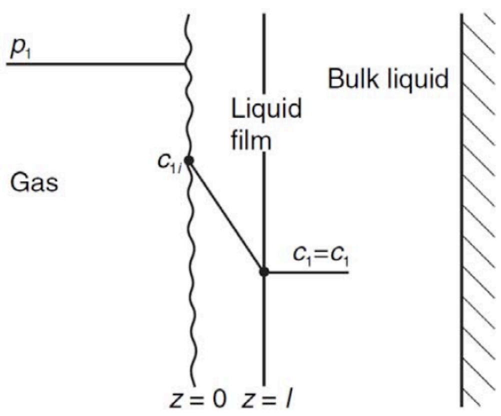
Goal: can we develop correlations from first principle which describes the following relationships

$$k \sim D^{0.5} \text{ or } D^{0.67}, \quad \sim v^{0.5} \text{ or } v^{0.67}$$

Three prominent mass transfer coefficient theories

Film theory

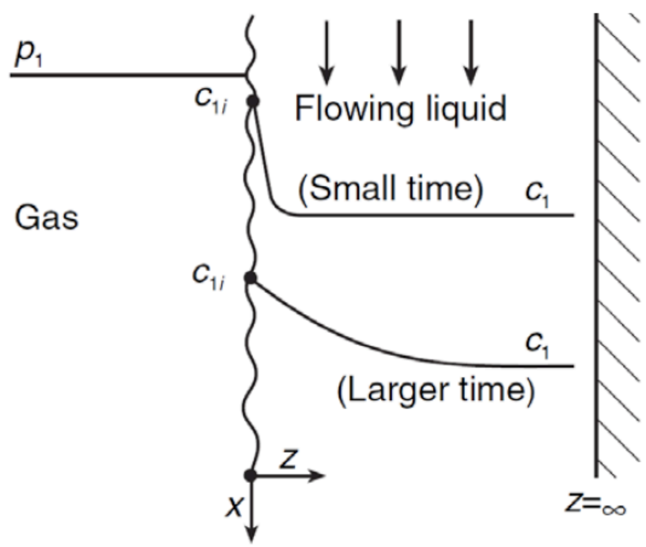
thin film diffusion



$$\frac{kl}{D} = 1$$

Penetration theory

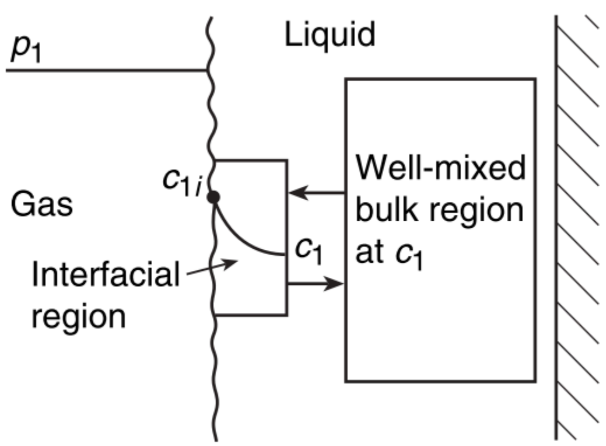
semi-infinite film diffusion



$$k = 2\sqrt{\frac{Dv_{max}}{\pi L}}$$

Surface renewal theory

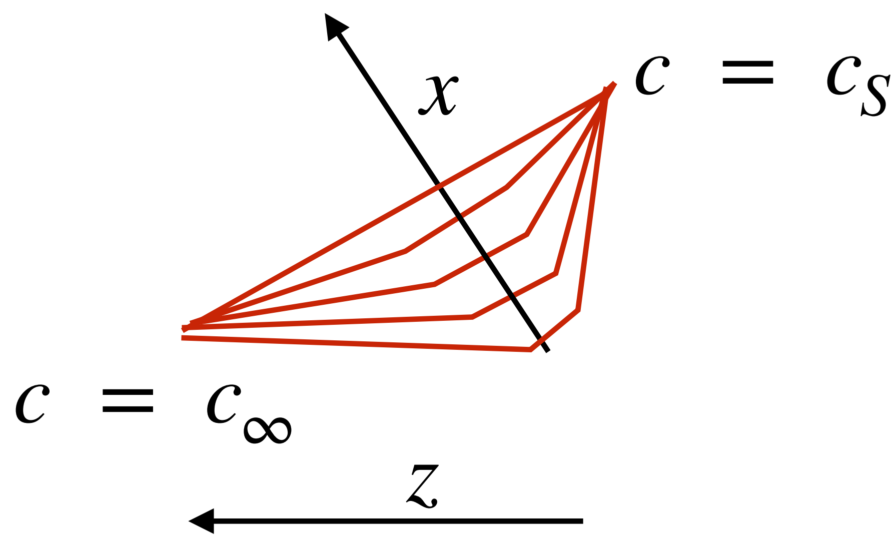
Surface layer is renewed by bulk flow or turbulence

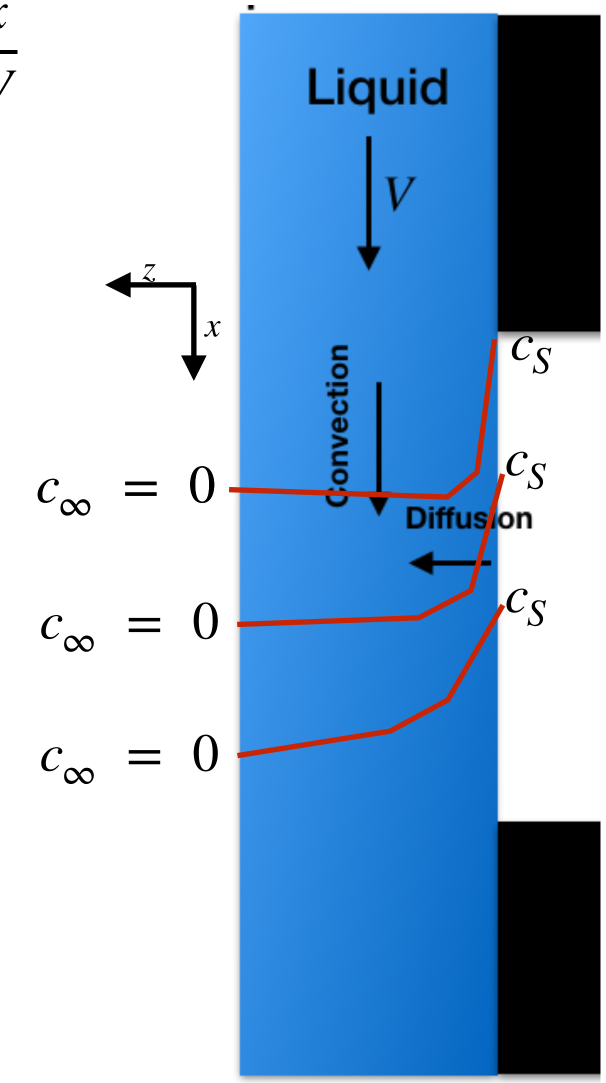


$$k = \sqrt{\frac{D}{\tau}}$$

Penetration theory: Gas diffusing in falling film

$$\frac{dc}{d\left(\frac{x}{V}\right)} = D\frac{d^2c}{dz^2} \qquad \frac{c(z,x) - c_S}{c_\infty - c_S} = erf\ \zeta \qquad \zeta = \frac{z}{\sqrt{4D\frac{x}{V}}}$$





Can you calculate the flux at z = 0 ?

Can you derive $k = 2\sqrt{\frac{Dv_{max}}{\pi L}}$

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Calculation of flux

$$\frac{c(z,x)-c_S}{c_\infty - c_S} = erf\,\zeta = \frac{2}{\sqrt{\pi}}\int_0^\zeta \exp(-r^2)dr \qquad J = -D\frac{\partial c}{\partial z}$$

$$\frac{\partial c}{\partial z} = \left(\frac{dc}{d\zeta}\right)\left(\frac{\partial \zeta}{\partial z}\right)$$

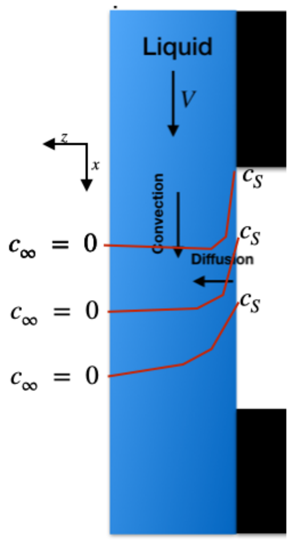
$$\Rightarrow \frac{dc}{d\zeta} = (c_\infty - c_S)\frac{2}{\sqrt{\pi}}\exp\left(-\frac{z^2}{4D(x/V)}\right) \qquad x/V = t$$

$$\zeta = \frac{z}{\sqrt{4D\frac{x}{V}}} \qquad \Rightarrow \left(\frac{\partial \zeta}{\partial z}\right) = \frac{1}{\sqrt{4D(x/V)}}$$

$$\Rightarrow \frac{\partial c}{\partial z} = (c_\infty - c_S)\frac{1}{\sqrt{\pi D(x/V)}}\exp\left(-\frac{z^2}{4D(x/V)}\right)$$

$$\boxed{\Rightarrow J = -D\frac{\partial c}{\partial z} = -\sqrt{\frac{D}{\pi(x/V)}}\,(c_\infty - c_S)\exp\left(-\frac{z^2}{4D(x/V)}\right)} \qquad J_{z=0} = \sqrt{\frac{D}{\pi(x/V)}}\,(c_s - c_\infty)$$

Calculation of average flux



$$J_{z=0} = \sqrt{\frac{D}{\pi(x/V)}}\ (c_s - c_\infty)$$

Integrating above over the entire length of the falling film, L

$$J_{z=0,average} = \frac{1}{L}\int_0^L \sqrt{\frac{D}{\pi(x/V)}}\ (c_s - c_\infty)dx$$

$$J_{z=0,average} = \frac{2}{L}\sqrt{\frac{DLV}{\pi}}\ (c_s - c_\infty)$$

$$J_{z=0,average} = 2\sqrt{\frac{DV}{\pi L}}\ (c_s - c_\infty) \quad = k(c_s - c_\infty)$$

$$k = 2\sqrt{\frac{DV}{\pi L}}$$

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Film theory: approximate the thickness of interface layer

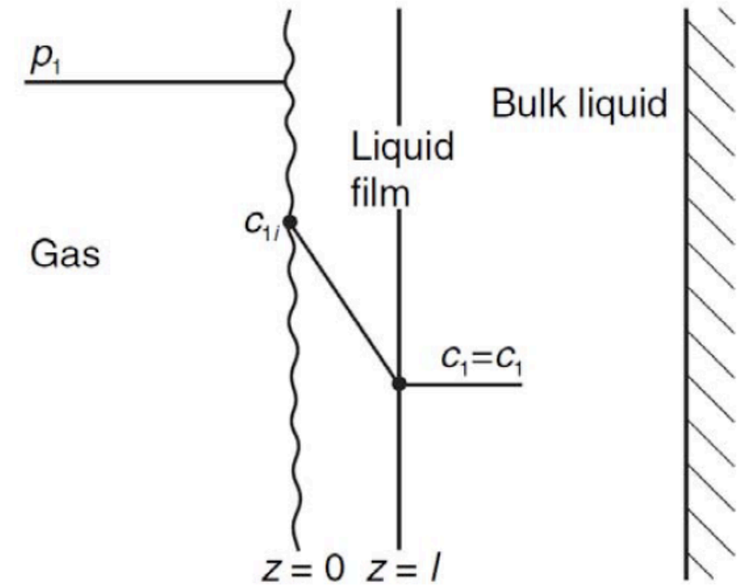
CO_2 is being absorbed out of a gas using water flowing through a packed bed with following data

- **CO_2 absorption rate is 2.3×10^{-6} mol/cm^{2}sec at 27 °C.**
- **Partial pressure of CO_2 in gas is 10 atm.**
- **Henry's law coefficient is 600 atm.**
- **D for CO_2 in water is 1.9×10^{-5} cm^2/sec.**
- **Assume bulk concentration of CO_2 in water to be zero.**

$$H = \frac{P_1}{x_{1i}}$$

$$N_1 = K_p(P_1 - Hx_1) = K_x\left(\frac{P_1}{H} - x_1\right)$$

$$\boxed{\frac{kl}{D} = 1}$$



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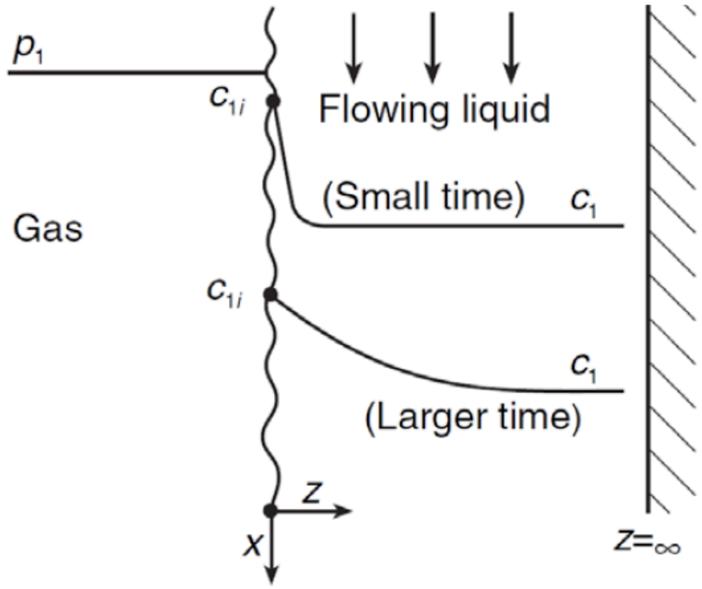
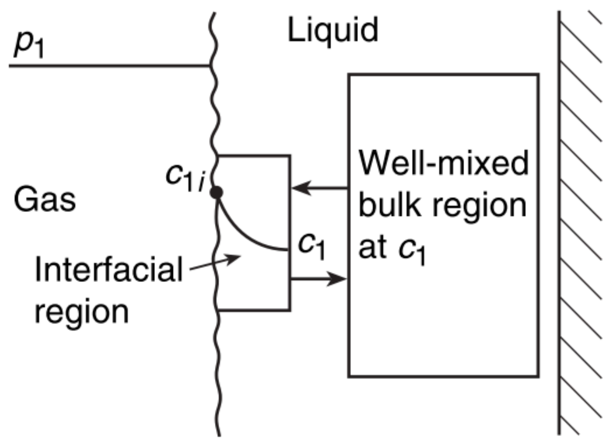
Penetration theory: approximate the contact time, L/v_{max}

Use the data from previous problem



Surface renewal theory: approximate the surface renewal time

Use the data from previous problem



Why theories fail (especially fluid-fluid)

Geometry is not well known.

Why theories fail: accounting for dead zones (where no mass transfer occurs)

If mass transfer is as per expected

$$\Rightarrow ka \ = -\frac{v}{L}\ln\left(\frac{c_{1L}^{ideal}}{c_{10}}\right)$$

In the case of fractional bypass

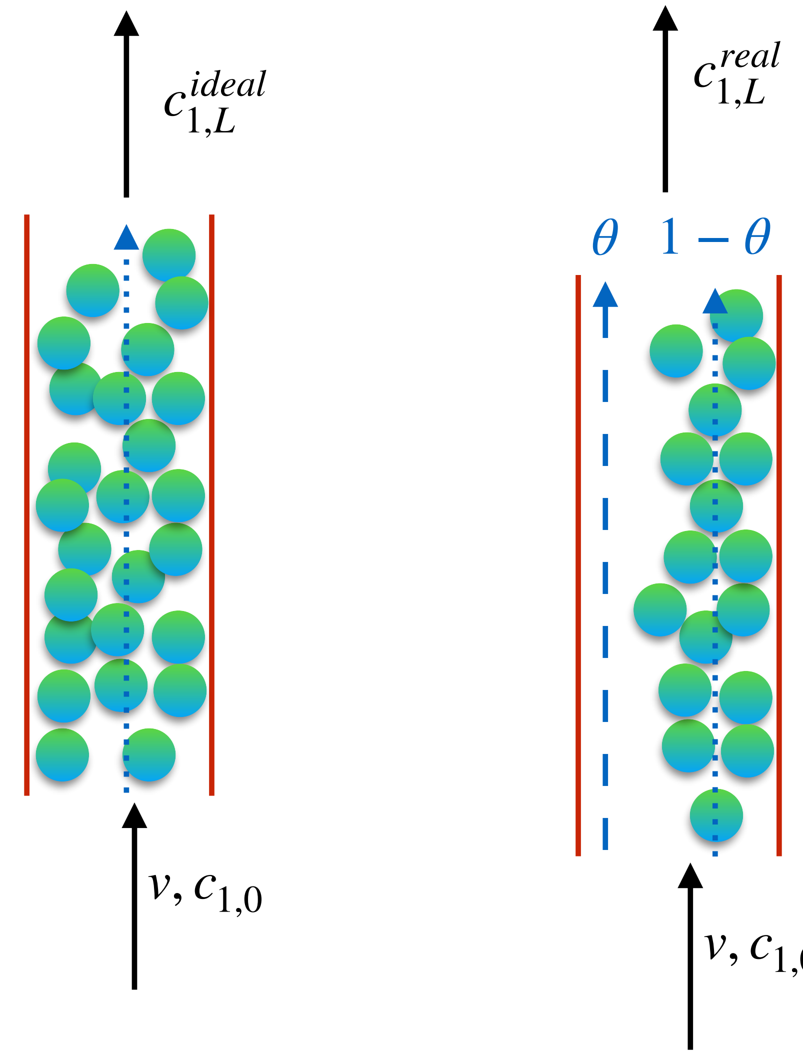
$$c_{1L}^{real} = \theta c_{10} \ + \ (1-\theta)c_{1L}^{ideal}$$

$$\theta = 0, \Rightarrow c_{1L}^{real} \ = c_{1L}^{ideal}$$

$$\Rightarrow k^{effective} \ = -\frac{v}{aL}\ln\left(\frac{c_{1L}^{real}}{c_{10}}\right)$$

$$\Rightarrow k^{effective} \ = -\frac{v}{aL}\ln\left(\frac{\theta c_{10} \ + \ (1-\theta)c_{1L}^{ideal}}{c_{10}}\right)$$

$$\Rightarrow k^{effective} \ = -\frac{v}{aL}\ln\left(\theta \ + \ (1-\theta)\frac{c_{1L}^{ideal}}{c_{10}}\right)$$



Only a part of flow is effectively contacted between liquid and gas.

Scrubbing of NH_3 by irreversible absorption

Mass transfer theories for concentration solutions

Restricting our arguments to dilute solution allows a focus on diffusion and a neglect the convection that diffusion itself can generate.

In dilute solution

$$N_1 = k(c_{1,i} - c_1)$$

In concentrated solution

$$N_1 = k(c_{1,i} - c_1) \ + \ c_{1,i} * v$$

Exercise problem 1:

NH_3 is being irreversibly absorbed in water using a packed bed contactor. The contactor height was designed to reduce NH_3 concentration by 100 fold. However, when experiments were carried out, the concentration only decreased by 10-fold. After some analysis, you found out that this could be because of bypass. Calculate the extent of bypass.

Exercise problem 2

You are doing a mass transfer related experiment for poorly soluble benzoic acid in water to use benzoic acid as a food preservative at 25 °C. For this, you added benzoic acid pellets at the bottom of the cylindrical water jar at t=0. The jar diameter is 10 cm. Its height is 20 cm and is completely filled with water. You carried two different experiments.

When there is no stirring, it takes 60 minutes to reach benzoic acid concentration 1.5 g/L at a height of 1 mm from the bottom. Concentration at the top of jar at 60 minutes was 0. Note that the concentration reaches 3 g/L everywhere after a very long time.

When there is vigorous stirring, benzoic acid concentration becomes 1.5 g/L in 5 minutes. Assume a uniform bulk concentration with stirring.

Calculate the mass transfer coefficient when stirring is used.

Also estimate
(i) the thickness of the boundary layer for mass transfer assuming the film theory for mass transfer coefficient, and
(ii) surface renewal time assuming the surface renewal theory for mass transfer.

$$\frac{c(z,t) - c_S}{c_\infty - c_S} = erf\,\zeta = \frac{2}{\sqrt{\pi}} \int_0^\zeta \exp(-r^2) dr$$

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